Determination of Nonvolatile Components in Polar Fractions of Rice Bran Oils

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ABSTRACT: High-oryzanol rice bran oil (HORBO), rice bran oil (RBO), and partially hydrogenated soybean oil (PHSBO) were used to prepare french fries. Polar fractions of the three oils were analyzed for nonvolatile components by high-performance size-exclusion chromatography (HPSEC) with ELSD. In all frying experiments, both HORBO and RBO yielded predominantly dimeric and monomeric materials. The concentrations of polymeric species in HORBO and RBO were greater than in PHSBO. The major degradation products from HORBO, RBO, and PHSBO were dimers (8.93 mg/100 mg oil), monomers (10.5 mg/100 mg oil), and DG (22.4 mg/100 mg oil), respectively. Thermal degradation *via* hydrolysis was much greater in PHSBO than in HORBO or RBO. Distribution data indicated that the extent of polymer formation from frying was in the order RBO > HORBO > PHSBO, consistent with the degree of lipid unsaturation and the oryzanol content in these oils. HPSEC-ELSD results from the two RBO showed that the amounts of various polymeric species, including trimers and higher polymers, were lower in HORBO than in RBO. The percentage of polar materials and the percentage of polymerized TG, which were used as indicators of oil quality and stability, decreased with increasing tocopherol and oryzanol contents in the order PHSBO > HORBO > RBO.

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KEY WORDS: Frying oil, high-oryzanol rice bran oil, high-performance size-exclusion chromatography, nonvolatile components, oil stability.

Fried foods are important food commodities produced by the food industry and convenience food-service restaurants. Because of the high temperatures used, frying processes are usually accompanied by thermolysis, hydrolysis, oxidative degradation, and polymerization (1,2). Frying oils are stabilized by partial hydrogenation or FA modification (3–5). Partial hydrogenation increases the saturated FA and *trans* FA contents and decreases the PUFA contents to produce more stable oil. However, undesirable effects of saturated and *trans* FA on cardiac health have been documented (6–8). Genetically modified oils containing high levels of favorable FA (e.g., high-oleic oils) can be used as alternatives to conventional frying oils (5) despite their inferior frying stability in comparison with hydrogenated oils. The search for ideal, good quality, stable oils for use in fried foods continues to present a formidable challenge and requires ingenious approaches to achieve the ultimate goal.

Rice bran oil is known to be effective in lowing blood cholesterol, and its phytosterol constituent γ-oryzanol has been reported as the active factor (9,10). γ-Oryzanol, which is derived from plant sterols, is a complex mixture of structurally related sterylferulate esters (Fig. 1) known to have antioxidative properties (11) and to inhibit oxidation in foods (12). Some plant sterols have been reported to suppress polymerization (13). Hence, the occurrence of the antipolymerization agent Δ^5-avenasterol in rice bran oil can be advantageous for frying foods. In view of the documented antioxidative/antipolymerization properties and the hypocholesterolemic/hypolipidemic activities of rice bran oil, it was worthwhile to conduct a comparative study on the stability of three oils during frying processes: high-oryzanol rice bran oil (HORBO), rice bran oil (RBO), and partially hydrogenated soybean oil (PHSBO). PHSBO was chosen because it is stabilized by partial hydrogenation, as mentioned, and is widely used in the fast-food industries. High-performance size-exclusion chromatographic (HPSEC) determinations (14–18) of nonvolatile components in polar isolates of frying oils have been valuable in providing information on oil deterioration. In this paper, the concentration of nonvolatile components in the selected frying oils and their

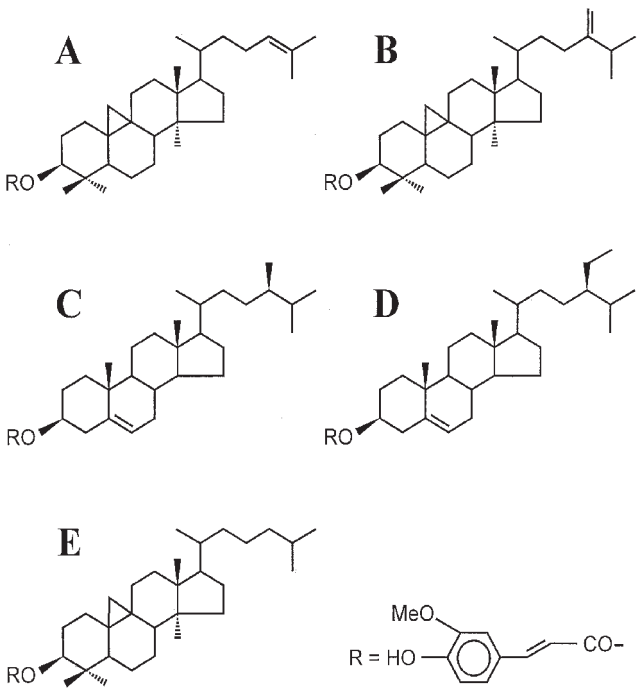

FIG. 1. Structures of major oryzanol components in rice bran oil. (A) Cycloartenol, (B) 24-methylenecycloartanol, (C) campesterol, (D) sitosterol, and (E) cycloartanol.

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distribution were evaluated by HPSEC-ELSD. The test oils also were assessed for their percentage of polar materials and percentage of total polymerized TG by silica gel column chromatography and gel-permeation HPLC, respectively.

EXPERIMENTAL PROCEDURES

Materials. Freshly refined, bleached, and deodorized (RBD) HORBO, RBD RBO, and RBD PHSBO were obtained from Riceland Foods (Stuttgart, AR). They were stored in a freezer prior to use. All zero-time oils (fresh, unused oils) had PV of 0.5, FFA values of 0.01%, and iodine values of 106. Calculated oxidizability values for HORBO, RBO, and PHSBO were 529, 527, and 544, respectively. The small differences in these values appeared to suggest this type of characterization had little merit. Oxidizability values are useful for predicting oil stability when oils having significantly different values are compared in the absence of antioxidants or antipolymerization agents. All test oils contained citric acid (50 ppm) when they were received, which had been added to the oils on the cooling side of deodorization during oil processing. Standards of oleic acid, monoolein, diolein, and triolein were obtained from Sigma (St. Louis, MO). Solvents and reagents for column chromatography, HPLC, capillary electrochromatography, and HPSEC were high-quality HPLC-grade products from Fisher Chemicals (Fairlawn, NJ).

Methods. FA compositions of the initial oils were determined in duplicate by capillary GC with a Varian Model 3400 chromatograph (Palo Alto, CA) equipped with an FID and a SP-2380 column (30 m × 0.25 mm i.d., 0.20 μm film thickness; Supelco, Bellefonte, PA). Column temperature was initially kept at 170°C for 10 min and then increased to 220°C at a rate of 3°C/min. Injector and detector temperatures were 240 and 280°C, respectively. Helium flow rate was 20 cm/s. Tocopherol and tocotrienol contents of the unused oils were determined in duplicate by normal-phase HPLC according to AOCS recommended practice Ja 13-91 (19). Total polymerized TG concentrations were determined in duplicate by gel-permeation HPLC, AOCS method Cd 22-91 (19).

Concentrations of polar compounds were determined in duplicate by a modified AOCS column chromatography method, Cd-20-91 (19). The method was modified as follows: Aliquot samples (1 g) of fried oils in duplicate were charged to a glass column filled with silica gel (25 g) and eluted with petroleum ether/diethyl ether (87:13) for the removal of nonpolar fractions, followed by chloroform/methanol (1:1) for the isolation of polar fractions. Chromatographic eluate fractions were monitored by TLC on a silica gel plate (0.025 × 20 × 20 cm) with hexane/diethyl ether/acetic acid (80:20:1, by vol) as the developing solvent. The TLC traces were visualized in an iodine chamber. As described in the AOCS procedure, a problem eluting with diethyl ether led to insufficient recovery (90–95.3%) of the polar materials. Therefore, chloroform/methanol (1:1) was used to elute the polar fractions in quantitative yield (99.5–100%).

Frying experiments were done in triplicate by adopting the procedures routinely used for preparing french fries in the fast-food service industry. Super Chef electric deep fryers (4″ × 8″ × 5″), Model EL414 (Super Chef Manufacturing Co., Houston, TX) were used for frying. Commercially frozen french-fried potatoes (crinkle-cut, 0.5″ thickness, 3 to 5″ long) were used as purchased from grocery stores, and they were void of any undesirable food additives such as synthetic or natural antioxidants. For each frying operation, french fries (250 g) were loaded in a kettle basket and fried at 191°C for 4 min. One batch was fried every 30 min and a total of seven batches (0.5 h initial heating +3.5 h frying = 4 h) were fried each day. Thus, test oils were subjected to intermittent frying at the constant temperature of 191°C, with a total heating/frying time of 168 h. Typically, frying commenced on day 1 with the test oils (2500 mL), each of which was filtered using a filter paper at the end of every frying day. On day 2 and thereafter, before frying recommenced, the used oils were replenished with fresh makeup oils (150–250 mL) to bring the oils back to the initial level. Samples (150 mL) of the filtered oils were withdrawn each day. Various assays were carried out on the samples collected for 6 d at intervals of 24 h heating/frying. Frying conditions such as amounts of makeup oil and consistency in food preparation often varied, causing irregularities in some experimental results.

RP-HPLC-UV of γ-oryzanol. The method used for the determination of γ-oryzanol was developed at Riceland Foods, so samples were analyzed at Riceland. All HPLC assays were performed on a Hewlett-Packard (Wilmington, DE) Model HP1100 chromatograph equipped with a built-in UV detector (325 nm) and HP ChemStation software for system control. The detector inlet was connected to a Supelco HPLC column (250 × 4.6 mm i.d.) packed with 5 μm Lichrosorb RP-18 octadecyl silica. A mobile phase consisting of water (1 L), acetic acid (10.1 mL), isopropanol (248.3 mL), methanol (2.246 L), and acetonitrile (2.3725 mL) was pumped through the column at a flow rate of 1 mL/min. Oil samples (0.5–5.0 g) in duplicate, liquified in a water bath at 60°C, were diluted to 10 mL with THF. Each of the upper layers was separated and filtered with a 0.45-μm filter vial. Aliquots (20 μL) were then injected onto the HPLC column for quantification. Calibration curves were constructed by plotting known amounts of γ-oryzanol in THF at concentrations ranging 50 to 1000 ppm against peak areas.

HPSEC-ELSD of nonvolatile components. HPSEC separations of nonvolatile components were carried out with a Thermo Separation Products (San Jose, CA) Model P4000 liquid chromatograph interfaced with a Sedex (Richard Scientific, Novato, CA) Model 55 ELSD. The detectors were coupled to three Polymer Laboratory (Amherst, MA) high-efficiency mixed-bed (100–1000Δ pore sizes) PLGEL MIXED-E columns (3 μm, 300 × 7.5 mm i.d.) connected in tandem. Analytical samples in THF (10–70 mg/mL) were injected onto the columns through a Thermo Separation Products autosampler and eluted with THF at a flow rate of 0.8 mL/min. Samples were prepared in duplicate, and triplicate analyses were performed. The mobile-phase eluent was recirculated through the HPSEC system and replenished with fresh solvent after 150–200 injections.

By using standards of known M.W. of oleic acid, monoolein, diolein, and triolein, a standard curve was constructed by plotting the logarithm of the M.W. of the standards against their retention times. HPSEC-ELSD peaks at retention times of monoolein, diolein, and triolein were designated as MG, DG, and monomers, respectively. Unknown nonvolatile components of dimers, trimers, and polymers were determined from the calibration data. Thus, the standard curve was extrapolated until it intercepted with the retention times of the unknown peaks to obtain their M.W. All quantification data were processed with Thermo Separation Products Model PC-1000 software. This data acquisition system generated a computer printout of each HPSEC-ELSD chromatogram on which the percentage compositions of nonvolatile components in the polar fractions of test oils were displayed. Concentrations (mg/100 mg oil) of the degradation products in the oils were then calculated from the percentage composition data based on the whole oils assayed.

Statistical analysis. Data from duplicate analyses were computed for SD and reported in the tables as relative SD (RSD).

RESULTS AND DISCUSSION

Table 1 shows the FA compositions and contents of tocopherols and tocotrienols of the three unused oils chosen for study. The two rice bran oils, HORBO and RBO, contained 42.4 and 42.7%, respectively, of oleic acid [18:1*c*9 (*cis* acid, double bond at the 9-position)] as the most abundant species (see footnote to Table 1 for code designations). Correspondingly, there were moderate levels, 37.2 and 36.8%, respectively, of linoleic acid [18:2*c,c* (*cis-cis* acid, double bonds at the 9- and 12 positions)] present in these oils. Fairly low percentages of linolenic acid (18:3) (HORBO, 1.47%; RBO, 1.22%) and traces of other unsaturated FA were detected in the rice bran oils. PHSBO had the acids 18:2*c,c* (32.2%) and 18:1*c*9 (29.5%) as the major species, along with 18:1*t*9 (*trans* acid, double bond at the 9-position) (6.34%), 18:1*c*13 (*cis* acid, double bond at the 13-position) (5.04%), and other unsaturated species as minor components. Although the three test oils contained generally low amounts of stearic acid 18:0 (<6.70%), 18:1*t*9 (<6.50%), and 18:3 (2.50%), these acids were present at higher levels in PHSBO than in HORBO and RBO. The combined percentages of various saturated acids in HORBO, RBO, and PHSBO were 17.94, 17.12, and 25.00%, respectively, whereas the percentages of the corresponding monounsaturated and diene FA were 43.28–37.41, 44.12–37.67, and 42.38–36.58%, respectively (Table 1). Evaluation of FA composition data for the initial oils aided in understanding the mode of and propensity for frying oil degradation. FA composition data were used to calculate oxidizability values and iodine values, which showed only slight differences among the three oils tested (Table 1).

The antioxidant data (Table 1) show that at zero time, α- and γ-tocopherols were present in varying amounts in all three oils and that PHSBO contained the highest level of total tocopherols (1131 ppm). Although the total tocopherol content of HORBO was about twice that of RBO, the former had a much lower level of tocotrienols than the latter (192 ppm vs. 962 ppm). Tocotrienols were not detected in PHSBO. The total concentration of tocopherols and tocotrienols in HORBO (463 ppm) was much lower than in RBO (1095 ppm) and PHSBO (1131 ppm). Since the antioxidants tocopherol and tocotrienol are believed to have a stabilizing effect on frying oils (20) in the absence of other complicating factors, their initial distribution in the oils would provide information to compare oil stability. Figures 2 and 3 show changes in the percentages of polar materials and polymerized TG, respectively, in the three test oils with frying time. The results of frying performance given in Figures 2 and 3 appear to show that the tocopherol antioxidants had some bearing on the quality of the test oils for the first 72 h of frying, during which PHSBO was more stable than the two rice bran oils. Presumably, lesser degrees of thermal oxidation and polymerization occurred in the presence of higher concentrations of the antioxidants in PHSBO during the early stage of frying.

Table 2 shows concentration data for oryzanol in HORBO and RBO. The different compositional distributions of

TABLE 1
FA Composition (%)[a] and the Content of Tocopherols and Tocotrienols (ppm) in Zero-Time Oils

Compound	HORBO	RBO	PHSBO
FA			
14:0	0.34	0.36	0.00
16:0	15.4	14.9	12.0
18:0	2.20	1.86	6.66
Total saturated acid	17.9	17.1	25.0
18:1*t*9	0.00	0.64	6.34
18:1*c*9	42.4	42.7	29.5
18:1*c*11	0.88	0.78	1.50
18:1*c*13	0.00	0.00	5.04
Total monoene acid	43.3	44.1	42.4
18:2*t,t*	0.00	0.00	0.92
18:2*c,t*	0.21	0.20	1.84
18:*t,c*	0.00	0.67	1.62
18:2*c,c*	37.2	36.8	32.2
Total diene acid	37.4	37.7	36.6
Total triene acid (18:3)	1.47	1.22	2.49
Total unsaturated acid	82.2	83.0	81.5
Tocopherols (T)			
αT	132	118	38.9
βT	ND	ND	ND
γT	139	4.64	1092
δT	ND	ND	ND
Total T	271	123	1131
Tocotrienols (T3)			
αT3	ND	148	ND
βT3	ND	ND	ND
γT3	192	814	ND
δT3	ND	ND	ND
Total T3	192	962	0.00
Total T + T3	463	1095	1131

[a]Composition is based on the area percentage. HORBO, high-oryzanol rice bran oil; RBO, rice bran oil; PHSBO, partially hydrogenated soybean oil; 18:1*t*9, *trans* acid, double bond at the 9-position; 18:1*c*9, *cis* acid, double bond at the 9-position; 18:1*c*11, *cis* acid, double bond at the 11-position; 18:1*c*13, *cis* acid, double bond at the 13-position; 18:2*t,t, trans,trans* acid, double bonds at the 9- and 12-positions; 18:2*c,t, cis,trans* acid, double bonds at the 9- and 12 positions. 18:2,*t,c, trans,cis* acid, double bonds at the 9- and 12-positions; 18:2*c,c, cis,cis* acid, double bonds at the 9- and 12-positions; ND, not detected. RSD values for the analysis of T and T3 averaged 4.2%.

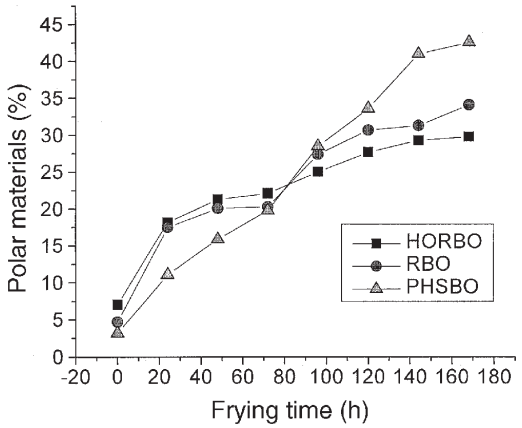

FIG. 2. Percentage of polar material in high-oryzanol rice bran oil (HORBO), rice bran oil (RBO), and partially hydrogenated soybean oil (PHSBO) after frying.

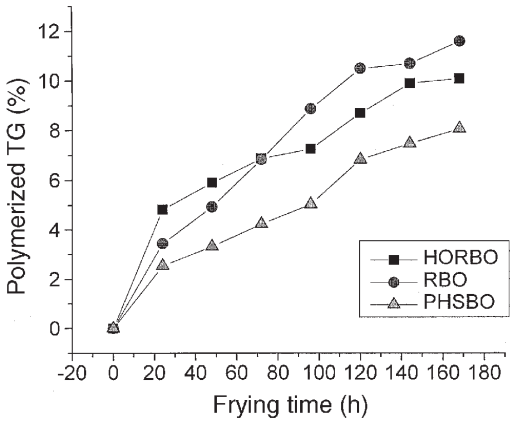

FIG. 3. Percentage of polymerized TG in HORBO, RBO, and PHSBO after frying. For abbreviations see Figure 2.

oryzanol components observed in the oils reflect the different refining processes used to obtain zero-time HORBO (a soda ash process using sodium carbonate) and RBO (a caustic process using sodium hydroxide). No oryzanol was added to the test oils. Initially, HORBO contained 0.74% total oryzanol, which was about 20 times more than that in RBO (0.036%). At 168 h, the total oryzanol contents in HORBO and RBO were 0.33 and 0.015%, respectively. Clearly, over the entire duration of frying (0–168 h), about one-half of the original content of oryzanol had degraded steadily, and a fairly constant ratio of the relative percentage of oryzanol was maintained for HORBO and RBO. Since HORBO and RBO were produced by different refining processes, the distribution of oryzanol in these oils differed. RBO had a concentration distribution of individual oryzanol components typical of generic rice bran oils (Table 2). On the other hand, HORBO showed components similar to RBO but at higher levels and with a different distribution. For HORBO, the oryzanol components had the following concentration distribution: campesterylferulate > cycloartenylferulate > sitosterylferulate/cycloartanylferulate > 24-methylene cycloartanylferulate. For RBO, the oryzanol components had the following concentration distribution: cycloartenylferulate > campesterylferulate > 24-methlene cycloartanylferulate > sitosterylferulate/cycloartanylferulate (Fig. 1). The relatively superior overall frying performance of HORBO might be attributed partly to the presence of high levels of oryzanol.

Under frying conditions simulating those used for frying french-fried potatoes in fast-food restaurants, the amount of polar material (Fig. 2) obtained at 168 h from HORBO (29.8%) was significantly lower than that found in PHSBO (42.6%), an obvious reversal from the percentage of polar material in the oils at zero time (HORBO, 7.05%, vs. PHSBO, 3.19%). After frying for 0 to 72 h, the amounts of degradation products formed in HORBO and RBO were consistently greater than those in PHSBO. Afterward (from 72 to 168 h), PHSBO underwent more extensive thermal decomposition than did both rice bran oils. Thus, during the later phase of frying, the oils appeared to deteriorate in the order PHSBO > RBO > HORBO (Fig. 2).

Figure 3 indicates that the order of polymerization at 168 h was RBO > HORBO > PHSBO. This observation may not be related to the slight but similar trend shown for differences in the monoene and diene FA compositions of the initial oils as well as their total unsaturated FA compositions (RBO,

TABLE 2
Oryzanol Concentrations (ppm) in Rice Bran Oils Used for French-Fried Potatoes[a]

Time (h)	HORBO					RBO				
	ST + CA	CP	MCA	CE	Total (%)	ST + CA	CP	MCA	CE	Total (%)
0	1197	3797	448	1993	0.74	48.5	101	88.6	121	0.036
24	794	2484	294	1318	0.49	36.1	66.8	53.7	85.9	0.024
48	651	2019	240	1072	0.40	29.3	56.1	42.3	74.8	0.020
72	630	1981	231	1061	0.39	26.6	46.8	34.0	66.1	0.017
96	556	1746	202	942	0.34	21.3	36.6	25.4	56.4	0.014
120	502	1571	181	849	0.31	20.8	36.0	25.1	56.9	0.014
144	473	1469	169	795	0.29	22.5	41.6	31.0	62.6	0.016
168	535	1686	193	904	0.33	22.3	38.6	27.2	58.2	0.015
AVRSD[b]	5.6	3.7	2.5	3.8		6.7	4.4	4.8	4.0	

[a]Analyzed by HPLC-UV.
[b]AVRSD, average relative SD (%); ST, sitosterylferulate; CA, cycloartanylferulate; CP, campesterylferulate; MCA, 24-methylene cycloartanylferulate; CE, cycloartenylferulate. Total (%) indicates the percentage of γ-oryzanol in an oil sample. For sample abbreviations, see Table 1.

83.0%, vs. HORBO, 82.2%, vs. PHSBO, 81.5%) (Table 1). The parallel trend in nominal variations between the unsaturated FA compositions and the polymer compositions in the zero-time oils might be fortuitous, based on their similarity in oxidizability and iodine values (Table 1). Although polymerization processes are initiated at the unsaturated FA moieties of TG, the presence of higher concentrations of tocopherols and oryzanol in PHSBO and HORBO (Tables 1 and 2) compared with RBO might have affected concurrent thermal oxidation and isomerization processes to form cyclic monomers, dimers, and polymers through polymerization.

Table 3 summarizes the concentrations of nonvolatile components in the polar fractions of the oils as determined by HPSEC-ELSD. A total of six major nonvolatile components were separated by HPSEC; these were tentatively designated as polymers (polymeric materials with M.W. greater than trimers), trimers, dimers, monomers, DG, and MG based on calibration with known standards (17). As a typical characteristic of HPSEC, the elution time of each of the nonvolatile components had an inverse relationship with the degree of polymerization or molecular mass. It must be clarified that the percentage of polymerized TG shown in Figure 3 does not approximate the total values of nonvolatile components tabulated in Table 3. The former excludes MG, DG, and monomers from the total values of polymerized TG. As shown from the results in Table 3, concentrations of polar decomposition products varied noticeably with frying times and oil varieties. HPSEC profiles (data not shown) of HORBO, RBO, and PHSBO exhibited similar peak patterns (17), in which peak intensities or analyte concentrations of the corresponding components increased gradually with increasing frying times. As expected, neither polymer nor trimer species were present in any of the unused oils at zero time. Furthermore, at zero time, dimer species were absent in both HORBO and RBO, although there were trace amounts of DG in HORBO but none in either RBO or PHSBO.

As shown in Table 3, with the exception of polymer species in HORBO and PHSBO, along with trimer species in PHSBO in the first 24 h, concentrations of degradation products increased as frying times increased from 0 to 168 h. At the completion of frying, both MG and DG were present in PHSBO (5.13 and 22.4 mg/100 mg oil, respectively) at substantially higher concentrations than in the two rice bran oils, HORBO (0.26 and 5.80 mg/100 mg oil, respectively) and RBO (0.15 and 4.98 mg/100 mg oil, respectively). Of the three oils, PHSBO had the greatest tendency to undergo hydrolysis, thermolysis, or other plausible decomposition processes to produce fragments of TG, presumably because the stabilizing effect of oryzanol apparent in the rice bran oils was absent in

TABLE 3
Nonvolatile Components in Polar Fractions of Frying Oils Used for French-Fried Potatoes[a]

Sample (h)	Component (mg/100 mg oil)						
	PM	TM	DM	MM	DG	MG	Total
HORBO							
0	ND	ND	ND	0.04	0.12	0.08	0.24
24	ND	0.15	1.99	2.57	1.05	ND	5.76
48	0.94	1.89	5.90	6.48	3.89	0.16	19.3
72	0.97	1.92	6.63	6.53	4.75	0.17	21.0
96	1.04	2.44	7.92	6.57	4.92	0.21	23.1
120	2.28	3.09	7.96	6.94	5.44	0.22	25.9
144	3.08	3.29	8.83	7.05	5.52	0.24	28.0
168	4.03	3.53	8.93	7.52	5.80	0.26	30.1
RBO							
0	ND	ND	ND	0.30	ND	0.05	0.35
24	0.54	1.20	5.89	6.21	2.71	0.06	16.6
48	0.97	1.78	6.92	6.81	3.66	0.08	20.2
72	1.15	1.85	7.09	6.90	3.70	0.09	20.8
96	3.13	3.14	8.25	8.34	4.45	0.10	27.4
120	3.80	3.55	9.11	8.82	4.51	0.11	29.9
144	4.14	3.60	9.61	9.49	4.93	0.13	31.9
168	5.19	3.87	10.0	10.5	4.98	0.15	34.7
PHSBO							
0	ND	ND	0.33	1.11	ND	0.17	1.61
24	ND	ND	0.70	1.13	0.35	ND	2.18
48	0.40	0.89	3.73	4.74	3.44	0.53	13.7
72	0.69	1.20	4.60	4.92	6.87	1.00	19.3
96	0.80	1.54	4.85	5.08	11.5	2.28	26.1
120	0.81	2.01	5.40	5.22	15.6	4.40	33.4
144	0.82	2.21	5.72	5.50	20.1	4.60	39.0
168	0.85	2.63	6.14	6.15	22.4	5.13	43.3
RSD[b] range	6.8–9.5	5.7–9.0	4.3–5.5	4.4–6.8	5.7–6.5	6.7–8.0	4.3–7.9

[a]Analyzed by high-performance size-exclusion chromatography-ELSD. For abbreviations and sample codes, see Table 1.
[b]RSD, relative SD (%). Nonvolatile components: PM, polymer species; TM, trimer species; DM, dimer species; MM, monomer species.

this oil. It must be reiterated that at zero time, either minute or nondetectable amounts of MG and DG were present in all three oils. In fact, DG were the most abundant nonvolatile component of the polar fraction of PHSBO when used for frying french-fried potatoes at 72 h or longer. Since polar fractions of the test oils were obtained by silica gel chromatography by removing nonpolar materials, including TG, monomer species in the polar fractions contained only the oxidized polar monomeric oxidized products derived from TG.

In the two rice bran oils, both monomers and dimers were present in equally high abundance in all samples collected at 24-h intervals throughout the frying times 24–168 h (Table 3). The monomer and dimer contents in HORBO were systematically lower than in RBO. On the other hand, PHSBO had the least amounts of monomers and dimers among the three oils analyzed. Similarly, at 168 h, the amounts of trimers in HORBO (3.53 mg/100 mg oil) and RBO (3.87 mg/100 mg oil) were fairly close in value, whereas PHSBO contained a slightly lower concentration of trimers (2.63 mg/100 mg oil) than the other two oils. A similar trend was observed for polymers, which were detected at a much lower level in PHSBO than in the two rice bran oils. Besides the initial PV, oxidation of the oils was measured indirectly from the percentage of polar materials, the percentage of polymerized TG, and the polymeric nonvolatile components, all of which served as indicators of oxidative stability of the test oils. Polymeric products were formed through concurrent oxidation and polymerization processes during frying. Thus, oxidation/polymerization of the test oils appeared to follow the order RBO > HORBO > PHSBO, even though differences among the test oils were small. These findings might partially reflect differences in both the unsaturated FA and antioxidant compositions of the test oils (Table 1). In other words, the potential of oils to deteriorate *via* oxidation and polymerization seemed to relate to the amount of tocopherol and oryzanol present, even though the differences in their oxidizability and iodine values were small. Such a relationship between tocopherol and oryzanol antioxidants and the formation of various polymeric compounds *via* oxidation or polymerization has not been described previously.

The frying characteristics of oils, as measured by the percentage of polar materials, the percentage of polymerized TG, and the distribution of nonvolatile components, can be used to assess oil quality and stability on a relative basis. HPSEC-ELSD evaluation of nonvolatile components allows one to differentiate the concentration distributions and degradation patterns of frying oils. Without additional evidence, it is unclear why thermal degradation *via* hydrolysis in PHSBO was greater than in HORBO or RBO. Further studies are needed to evaluate the sensory properties of french fries cooked in these oils and to characterize the degradation products of sterols and tocol antioxidants in order to understand the overall frying performance of quality oils.

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